



High performance solid-state supercapacitor with PVA–KOH–K₃[Fe(CN)₆] gel polymer as electrolyte and separator

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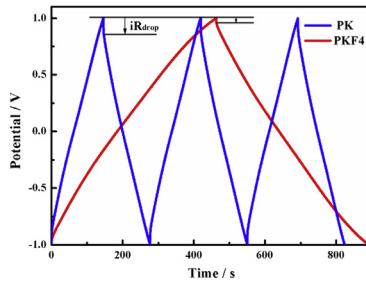
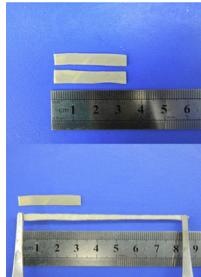
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HIGHLIGHTS

- Alkali and potassium ferricyanide doped polyvinyl alcohol gel electrolyte is prepared.
- The PVA–KOH–K₃[Fe(CN)₆] gel electrolyte can also be used as separator.
- The introduction of K₃[Fe(CN)₆] increases the ionic conductivity of electrolyte.
- The supercapacitor exhibits flexible and wide potential window properties.

GRAPHICAL ABSTRACT



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ABSTRACT

A gel polymer PVA–KOH–K₃[Fe(CN)₆] is prepared by potassium hydroxide and potassium ferricyanide doped polyvinyl alcohol, and a solid-state supercapacitor is assembled using the gel polymer as electrolyte and separator, activated carbons as electrode. The gel polymer exhibits flexible, high ionic conductivity and wide potential properties. The electrochemical properties of the supercapacitor are investigated using cyclic voltammetry, galvanostatic charge/discharge, and impedance spectroscopy techniques. The electrode specific capacitance of the supercapacitor can be as high as 430.95 F g⁻¹, and after 1000 cycles at a current density of 1 A g⁻¹ it still remains higher than 380 F g⁻¹. The energy density and power density of the supercapacitor reach 57.94 Wh kg⁻¹ and 59.84 kW kg⁻¹, respectively. These novel flexible gel polymers are desirable for applications in supercapacitor devices.

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1. Introduction

In the 21st century, one of the greatest challenges is unquestionably energy storage and conversion. As the concern grows over fossil fuel usage, in terms of global warming and resource depletion, there will be a progressive swing to renewable energy. This will necessitate the development of improved methods for storing

electricity when it is available and retrieving when it is needed [1]. Over the past few years, supercapacitor as an energy conversion/storage system have ignited significant worldwide investigation, because of their great advantages including large specific capacitance, rapid charging/discharging rates, fast energy delivery, high power performance, long cycle life, and environment-friendly features [2–6]. The high power density of supercapacitor is leading to their application in various other novel devices for load leveling, hybrid capacitor-battery systems, cold-start assistance, and catalytic converter preheating [7].

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Electrolyte plays a critical role in supercapacitor, the ionic conductivity and potential range of the electrolyte can influence supercapacitor performance [8,9]. Most of the reports on supercapacitor are based on liquid electrolytes [10–12]. Liquid electrolytes possess high ionic conductivity but low potential range (limited to ~1.0 V) in power sources. But more importantly, these are associated with the similar disadvantageous problems as observed in the liquid electrolytes, such as leakage, corrosion and explosions [13–15]. Therefore, replacing liquid electrolytes with solid electrolytes in supercapacitor has been explored by many researchers. The solid electrolytes have several advantages over liquid ones that includes easy handling without spillage of hazardous liquid and thus making it environmentally safe, low internal corrosion, simple principle and mode of construction, flexibility in packaging etc. [16–18]. Recently, Supercapacitor based on gel polymer electrolytes have been explored by several authors, such as PVA–H₃PO₄ [19], PVA–H₂SO₄ [20], gelatin–acetic acid [21], PAA–KCl [22], PEG–PMMA–EMI–TFSI(1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide) [23] and PVA–KOH [24].

Potassium ferricyanide (K₃[Fe(CN)₆]), a bright red salt consists of the coordination compound [Fe(CN)₆]³⁻, has been used as an electrochemical probe reagent in studying the electrochemical characteristics of electroactive substances, such as the reversibility electrode reaction process, chemical reaction process, electrode's adsorption surface area and determining medicaments [25–28]. Due to its oxidability, potassium ferricyanide also plays an important role in chemiluminescence [29–31]. As far as we know, there are scanty reports on gel polymer consisting of K₃[Fe(CN)₆] blended with PVA and KOH.

In the present work, a flexible gel polymer PVA–KOH–K₃[Fe(CN)₆] was prepared by adding K₃[Fe(CN)₆] and KOH to PVA, and a solid-state supercapacitor was assembled using the gel polymer as electrolyte and separator, activated carbon as electrode. The electrochemical properties of the solid-state supercapacitor were characterized by cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy techniques. In addition, the performance of this supercapacitor is compared with that of the supercapacitor with PVA–KOH gel polymer. Electrochemical tests indicate that the supercapacitor with PVA–KOH–K₃[Fe(CN)₆] gel polymer exhibit very high electrode specific capacity (430.95 F g⁻¹) and excellent cycling stability.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, Aladdin Co., China, molecular weight 44.05 MW, alcoholysis: 99.8–100%), KOH (Sinopharm Chemical Reagent Co., China), K₃[Fe(CN)₆] (Tianjin Guangfu Technology Development Co., China), Activated carbon (AC, Shanghai Sino Tech Investment Management Co., China). All other chemical reagents were in analytical grade.

2.2. Preparation of gel polymer

Gel polymer PVA–KOH–K₃[Fe(CN)₆] was prepared in solution-casting method by modifying the procedure from the previous literature [24]. First, 1 g PVA and 1 g KOH was dissolved in some deionized water with agitation at 85 °C for 5 h. After complete dissolution, the resulting solution was continuously stirred until it took on a homogeneous viscous appearance. Then, the mixture was poured to glass petri dishes and the excess water was evaporated at room temperature. Thus a free-standing thick PVA–KOH gel polymer was obtained and named PK. A series of ternary PVA–KOH–

K₃[Fe(CN)₆] gel polymer were prepared by dissolving PVA, KOH and K₃[Fe(CN)₆] with controlled weight ratio. Respectively, PVA/KOH/K₃[Fe(CN)₆] was 1:1:0.01, 1:1:0.02, 1:1:0.04, 1:1:0.06 and 1:1:0.1, followed by the same method above. The gel polymer electrolytes obtained at the different ratios were denoted as PKF1, PKF2, PKF4, PKF6 and PKF10.

2.3. Preparation of activated carbon electrode

To prepare the electrode, the uniform slurry of AC, acetylene black and binder PTFE aqueous solution in the weight ratio 80:10:10 was fully ground in an agate mortar and bound with ethanol at room temperature [32]. After ultrasonic vibration, the obtained slurry was coated on the nickel foam substrate, dried, and pressed under a pressure of 20 MPa to make a thin slab with a thickness of about 0.2 mm [33]. After being dried at 60 °C for 24 h, an AC electrode thus was obtained.

2.4. Supercapacitor assembly

A supercapacitor was fabricated by sandwiching the gel polymer between a pair of the AC electrodes as shown in Fig. 1. The gel polymer simultaneously served as electrolyte and separator.

2.5. Characterizations

The gel polymer deformation was tested via bending and stretching. The membrane of the gel polymer was cut into a ribbon of 0.5 cm width and 3.3 cm length and the deformation was described under the action of applied forces.

All electrochemical measurements (CHI 660D, Chenghua, Shanghai, China) of the supercapacitor were conducted using a two-electrode system under ambient conditions.

The cyclic voltammetry (CV) measurements were done in the potential range of -1 to 1 V at various scan rates from 5 to 100 mV s⁻¹. The galvanostatic charge/discharge (GCD) property was measured at the current densities of 0.5, 0.8, 1, 2, and 3 A g⁻¹ with cut off voltage of -1 to 1 V. The electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency ranging from 100 mHz to 100 kHz with a bias voltage of -1, 0, and 1 V. Measurement of cycle-life stability were performed using computer controlled cycling equipment (LAND CT2001A, Wuhan, China).

The supercapacitor specific capacitance (C, F g⁻¹) and electrode specific capacitance (C_s, F g⁻¹) were evaluated from charge/discharge curves according to the following equation [34,35]:

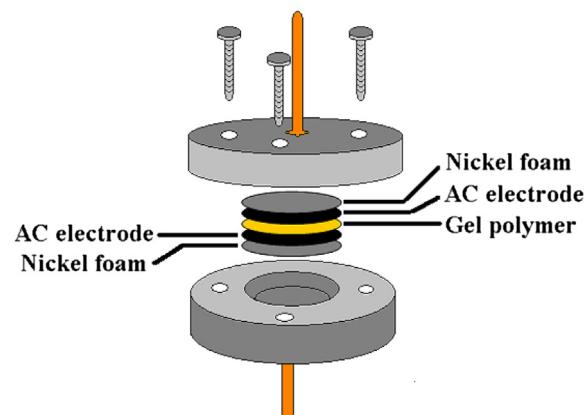


Fig. 1. Schematic representation of the supercapacitor.

$$C = (I \times \Delta t) / (\Delta V \times m_{ac}) \quad (1)$$

$$C_s = 4 \times C \quad (2)$$

Energy density (E , Wh kg $^{-1}$), equivalent series resistance (ESR) and power density (P , kW kg $^{-1}$) of the supercapacitor were calculated according to the following equations [35,36]:

$$E = \left[(C \times (\Delta V)^2) / 2 \right] \times (1000 / 3600) \quad (3)$$

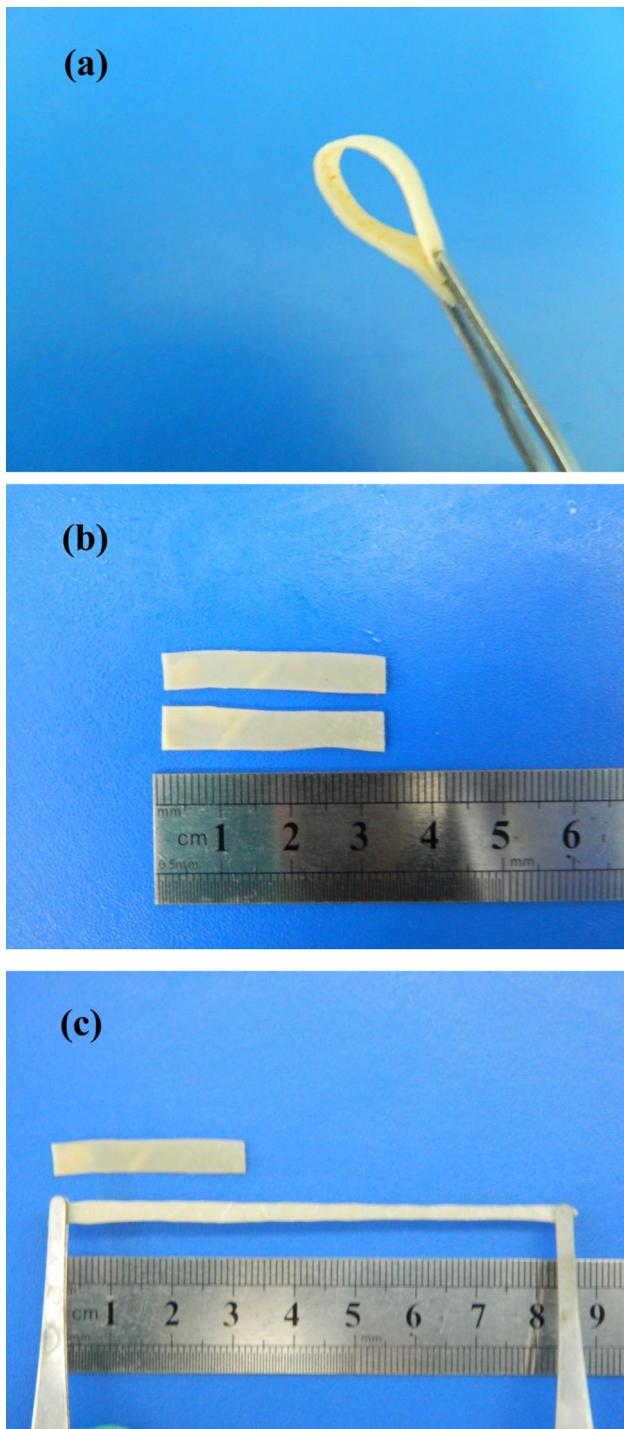


Fig. 2. Photographs of flexible PVA–KOH–K₃[Fe(CN)₆] gel polymer.

$$ESR = iR_{drop} / (2 \times I) \quad (4)$$

$$P = (\Delta V)^2 / (4 \times ESR \times m_{ac}) \quad (5)$$

where I (ampere) is the discharge current, m_{ac} (grams) is the weight of active material (including the binder and the graphite), Δt (seconds) is the discharge time, ΔV (volts) represents the operating voltage window of the supercapacitor, and iR_{drop} (volts) is defined as the electrical potential difference between the two ends of a conducting phase during charging/discharging.

Besides, ionic conductivity of the gel polymer in the supercapacitor was also determined from impedance spectrum. The ionic conductivity (Ω , S cm $^{-1}$) of gel polymer can be calculated by the following equation [37]:

$$\sigma = L / (R_b \times S) \quad (6)$$

where L (cm) is the distance between the two stainless steel sheets, R_b (ohms) is the bulk resistance, S (cm 2) is the contact area of the electrolyte film with stainless sheets during the experiment.

3. Results and discussions

3.1. Mechanical properties of the gel polymer

The PVA–KOH–K₃[Fe(CN)₆] gels polymer have excellent bending and stretching properties. From Fig. 2(a) it can be observed, the gel polymer ribbon is easy bent into a circular arc, and do not fracture even when they are bent over 180°, and in Fig. 2(b) and (c), the gel polymer ribbon can be elastically stretched to about 2.5 times length than its original. The ribbon quickly recovered its original shape after the external force was removed.

3.2. Ionic conductivity of gel polymer

The ionic conductivity of gel electrolyte affects the supercapacitor performance. Fig. 3 illustrates the dependence of the conductivity on K₃[Fe(CN)₆] content in the gel polymer at room temperature. It is observed that the ionic conductivity of PK system (K₃[Fe(CN)₆] mass at 0.00 g) is lower than that of PKF system. For the PKF gel polymer system PK1, PK2, PK4, PK6 and PK10, the ionic conductivity values increases with the corresponding K₃[Fe(CN)₆] content up to 0.01, 0.02 and 0.04 g, respectively. However, when

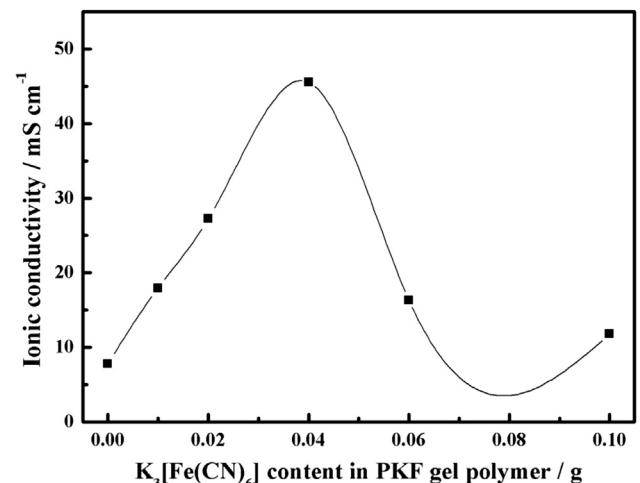
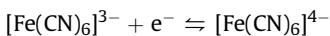


Fig. 3. Ionic conductivity of PKF gel polymer with different content of K₃[Fe(CN)₆] (PVA = 1 g, KOH = 1 g).

$K_3[Fe(CN)_6]$ content is 0.04 g, the ionic conductivity reaches the best value (45.56 mS cm^{-1} , according to the Eq. (6)). But, when the $K_3[Fe(CN)_6]$ content beyond 0.04 g, the ionic conductivity decreases with the increase of $K_3[Fe(CN)_6]$ content, because higher $K_3[Fe(CN)_6]$ content will lead to the aggregation of free ions and the crystallization of $K_3[Fe(CN)_6]$ in PVA system, which decreases the ionic conductivity of the gel polymer electrolyte [38].

3.3. Cyclic voltammetry

Cyclic voltammetry for the supercapacitor with gel polymer PK and PKF4 at scan rate of 100 mV s^{-1} in the potential window range -1 to 1 V are presented in Fig. 4. The supercapacitor with PK shows a fusiform without any obvious redox peaks, which indicates that the supercapacitor possesses a typical electrical double-layer capacitance. But, when the $K_3[Fe(CN)_6]$ is added to the PVA–KOH, the supercapacitor shows a rectangular CV curve with a pair of broad and symmetric redox peaks centered at around 0 V . The appearance of the redox peaks are attributed to the $K_3[Fe(CN)_6]$ that causes a redox processes on the electrolyte|electrode interface [39], and therefore gave rise to pseudocapacitance of the electrode. Since the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ has a good reversible redox specialty, which has been applied in electrical double-layered capacitors with liquid electrolytes [40], when $K_3[Fe(CN)_6]$ is doped in the PVA–KOH in the charge process, the $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ is formed, and a reversible redox reaction occurs. The redox process in the electrolyte|electrode can be presented as follows:



CV curves for various mass ratios of $K_3[Fe(CN)_6]$ to PVA–KOH are given in Fig. 5. All the supercapacitors exhibit rectangular CV curve behavior and wide oxidation and reduction waves centered at around 0 V , which suggests that their capacitance predominantly arises from combination of electrical double layer capacitance (EDLC) via accumulation of charges at the electrode|electrolyte interface and pseudo-capacitance through reversible redox reaction from $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ [41]. When $K_3[Fe(CN)_6]$ content is 0.01 and 0.02 g, the CV curves of the area have increased a lot. Therefore, the electrochemical properties of the supercapacitors with PKF1 and PKF2 are better presented than the supercapacitor with PK. As the $K_3[Fe(CN)_6]$ content increases to 0.04 g, a maximum CV curve area of the supercapacitor is obtained. However, it is found that the CV curve area of the supercapacitor decreases when

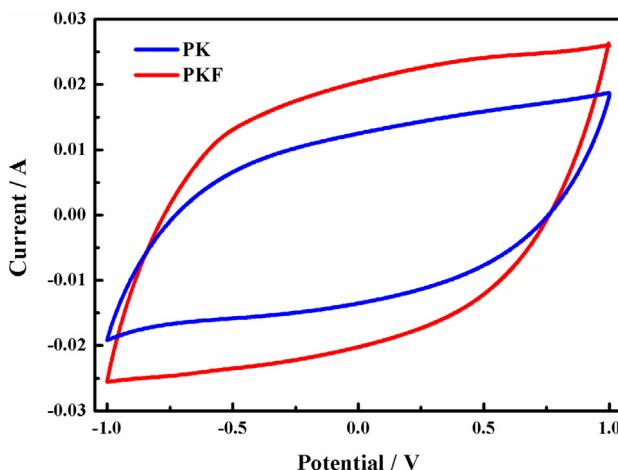


Fig. 4. Cyclic voltammetry for the supercapacitors with gel polymer PK and PKF4 at scan rate of 100 mV s^{-1} in the potential window of -1 to 1 V .

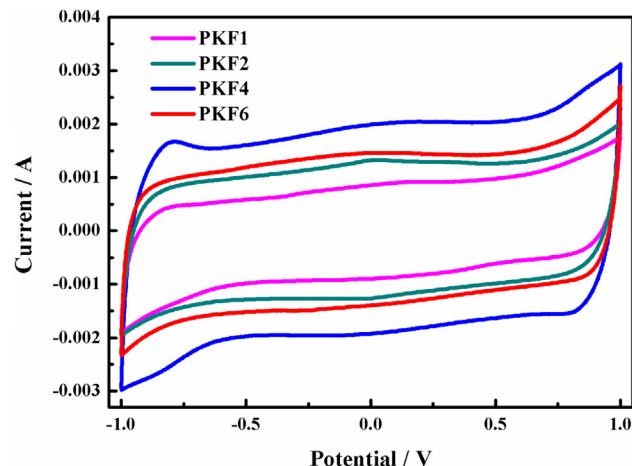


Fig. 5. Cyclic voltammograms for the supercapacitor with PKF gel polymer at different $K_3[Fe(CN)_6]$ content (wt%) and scan rate of 5 mV s^{-1} .

the $K_3[Fe(CN)_6]$ content becomes 0.06 g. The presence of a large number of $K_3[Fe(CN)_6]$ in the gel polymer can result in the crystal precipitation, and the $K_3[Fe(CN)_6]$ crystal itself does not contribute to the ionic conductivity. Therefore, the decrease in the CV curve area is because a large amount of $K_3[Fe(CN)_6]$ does not integrate into the gel polymer, and excess of the $K_3[Fe(CN)_6]$ will prevent the transfer of electrons and gathering the charge.

Fig. 6 presents CV curves for the supercapacitor based on PKF4 gel polymer at the different voltage scan rates. The supercapacitor shows pronounced current response over the potential window. At a lower scan rate (5 mV s^{-1}), the supercapacitor gives a voltammogram close to a standard rectangular shape, which is the characteristic of an activated carbon supercapacitor. At a higher scan rate (10 – 100 mV s^{-1}), the shapes remain close to the standard rectangular which suggests the supercapacitor has a very excellent stability.

3.4. Galvanostatic charge/discharge measurements

The galvanostatic charge/discharge is a reliable method to evaluate the electrochemical capacitance of materials. Fig. 7 shows the galvanostatic charge/discharge curves of supercapacitor with PK and PKF4 gel polymer at a current density of 500 mA g^{-1} at room

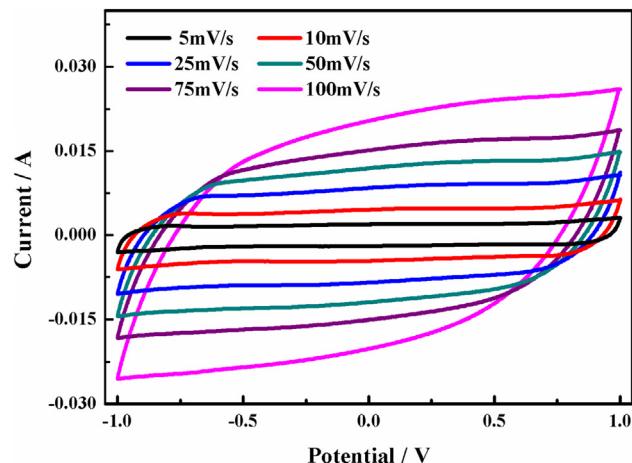


Fig. 6. Cyclic voltammograms for the supercapacitor with PKF4 gel polymer at different scan rates from 5 mV s^{-1} to 100 mV s^{-1} .

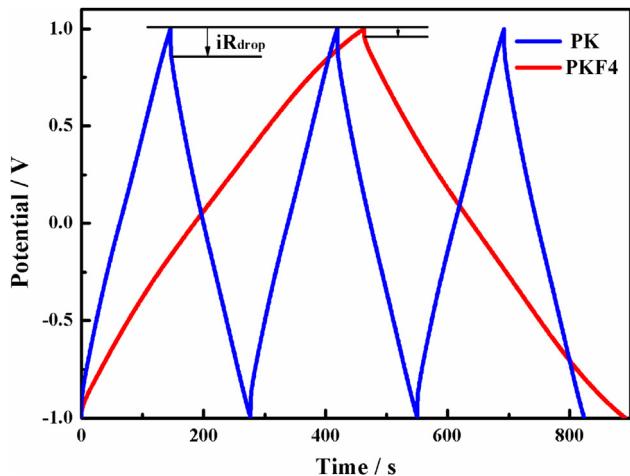


Fig. 7. Charge–discharge curves of supercapacitor with PK and PKF4 gel polymer at a current density of 500 mA g^{-1} .

temperature. Obviously, the charge–discharge time of the supercapacitor with PKF4 is much longer than that the supercapacitor with PK. The supercapacitor with PKF4 gel polymer exhibits smaller iR_{drop} than the supercapacitor with PK gel polymer, and the ESR are calculated as 4.42 and $19.23 \Omega \text{ cm}^2$, respectively [17,21]. It is due to the PKF4 gel polymer has higher ionic conductivity than the PK gel polymer shown in Fig. 3.

It can be seen the charge curve of supercapacitor with PKF4 is almost linear and symmetrical to their discharge counterparts, revealing a great of improvement by $\text{K}_3[\text{Fe}(\text{CN})_6]$ on the electrochemical performances of the supercapacitor. Longer charge–discharge time for the PKF4 than PK may be due to the additional contribution of reversible redox process by $\text{K}_3[\text{Fe}(\text{CN})_6]$, which has been interpreted aforementioned. So, the total capacitance of the supercapacitor consists of electrical double layer capacitance from the ions on the surface of activated carbon electrode and pseudo-capacitance through reversible redox reaction from $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ on the electrolyte|electrode interface.

According to Eq. (2), for a charging/discharging current density of 500 mA g^{-1} , discharging specific capacitance of the electrode for the supercapacitors with PK and PKF4 are determined to be 137.80 and 430.95 F g^{-1} , respectively. Obviously, the C_s of the supercapacitor with PKF4 is larger than that of the supercapacitor with PK gel polymer. The electrode discharging specific capacitance for the PKF4 is increased by 293.15 F g^{-1} compared to the current PK system. It is concluded that the redox mediator can greatly improve the capacitive property of the supercapacitor.

Fig. 8(a) presents the charge/discharge curves of the supercapacitor with PKF4 at various current densities of 0.5, 0.8, 1, 2 and 3 A g^{-1} . The discharge capacitances at various current densities are plotted in Fig. 8(b). It is evident that the capacitance of the supercapacitor slowly decreases as the current density becomes larger. Significantly, even at a current density as high as 3 A g^{-1} , the electrode specific capacitance can still achieve to 322.80 F g^{-1} , which remains approximate to 75% of the highest specific capacitance. The result indicates the excellent electrochemical properties of the supercapacitor with PKF4 can be maintained under high current density and it has better rate capability than the supercapacitor with PK.

The energy and power densities were derived from galvanostatic charge/discharge at various current densities. According to Eqs. (3) and (5), energy density and power density of the supercapacitor with PKF4 gel polymer is 57.94 Wh kg^{-1} and 59.84 kW kg^{-1} , respectively. Compared with the current gel

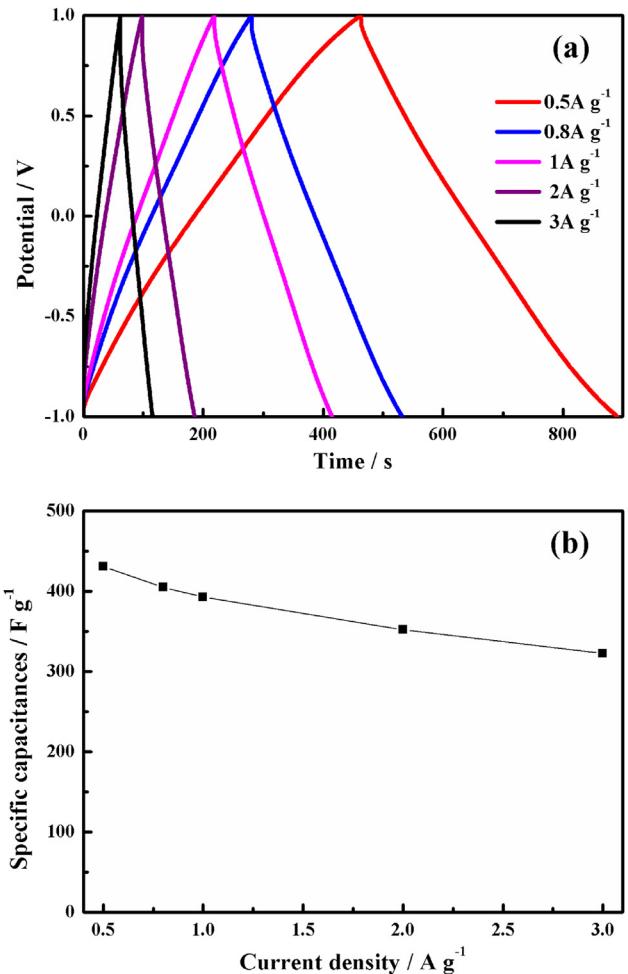


Fig. 8. (a) Galvanostatic charge/discharge curves of supercapacitor with PKF4 gel polymer at various current densities; (b) Discharge capacitances at various current densities.

polymer PK [24], the PKF4 has excellent electrochemical properties of high energy density and power output. These detailed comparison parameters for two electrolytes are listed in Table 1.

3.5. EIS technique

In order to investigate the electrochemical behavior at the electrode|electrolyte interface in detail, EIS measurements were employed. Fig. 9(a) shows the Nyquist plots for the supercapacitors with PK and PKF4 gel polymer. They both have ideal electrochemical capacitance behavior, i.e., imaginary parts of impedance at low frequency region are nearly linear [42,43], a small depressed semicircle at higher frequency [44]. From the enlarged view of the higher frequency semicircles, it can be seen that the supercapacitor with PKF4 not only has lower inner resistance (R_i , $1.29 \Omega \text{ cm}^2$), calculated from the point of intersecting with the x-axis in the range of high frequency, but also has smaller charge transfer

Table 1
Characteristic parameters for supercapacitor with different gel polymer from GCD.

Electrolyte	$C_s (\text{F g}^{-1})$	ESR ($\Omega \text{ cm}^2$)	$E (\text{Wh kg}^{-1})$	$P (\text{kW kg}^{-1})$
PK	137.8	19.23	20.85	12.20
PKF4	430.95	4.42	57.94	59.84

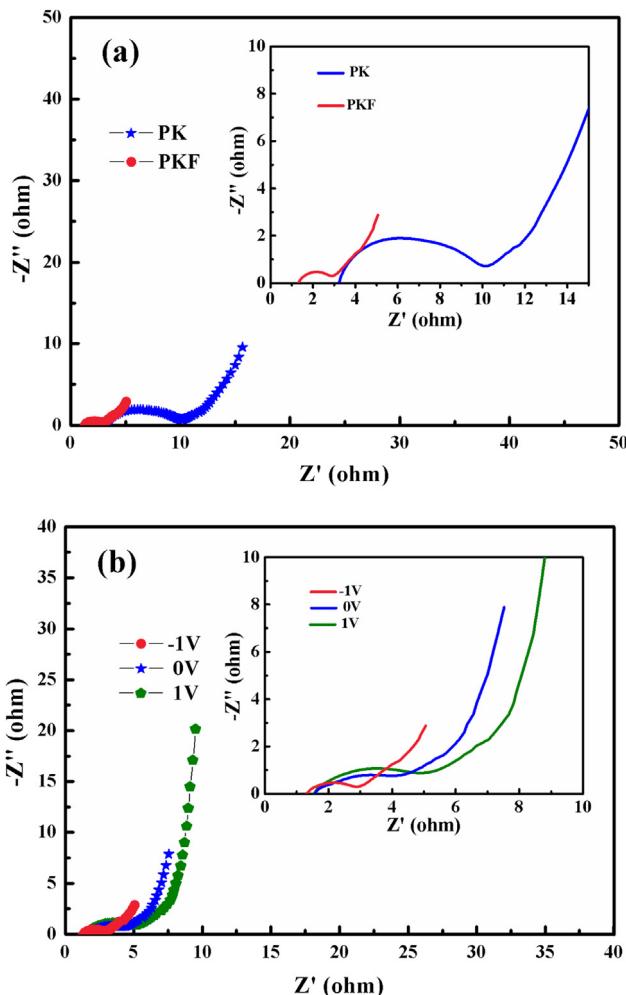


Fig. 9. (a) EIS of supercapacitors with PK and PKF4 gel polymer, the close-up view of the left plot in high-frequency region. (b) EIS at -1 , 0 , and 1 V bias voltage on the supercapacitor with PKF, the close-up view of the left plot in high-frequency region.

resistance (R_{ct} , $0.24 \Omega \text{ cm}^2$), counted from the span of the single semicircle along the x -axis from high to low frequency. Hence, the $\text{K}_3[\text{Fe}(\text{CN})_6]$ can enhance the ionic conductivity of gel polymer and the interaction of electrode|electrolyte interface, which results in good electrochemical performance for PVA–KOH– $\text{K}_3[\text{Fe}(\text{CN})_6]$ system.

Moreover, the EIS of the supercapacitor with PKF4 gel polymer at different bias potentials from -1 to 1 V is shown in Fig. 9(b). It can be seen that the R_{ct} decline with the increase of bias potential, demonstrating the existence of redox reaction in this potential region [6,45].

3.6. Cycle-life testing

Cyclic durability is one of the most significant electrochemical performances of supercapacitor. The cycling stability of the supercapacitors based on PK and PKF4 gel polymer were measured by charge/discharge cycling at a current density of 1 A g^{-1} , as depicted in Fig. 10. It is seen that the supercapacitor with PKF4 gel polymer has a good retention of 89.3% of its initial electrode specific capacitance after 1000 cycles, showing good stability for a long cyclic life. However, the supercapacitor with PK has worse cycle-life stability, after 1000 charge/discharge cycles the electrode specific capacitance remains only 48.1% , compared to the begin state. It is

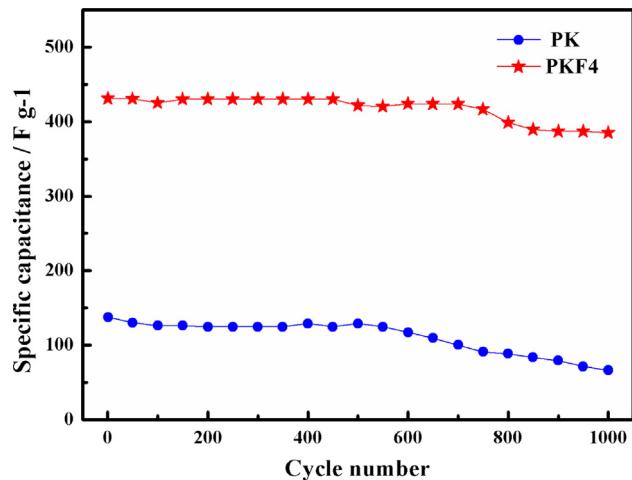


Fig. 10. Variations of the electrode specific capacitances of supercapacitors with PK and PKF4 gel polymer as a function of cycle number measured at the charge/discharge current density of 1 A g^{-1} .

obvious that the PKF4 gel polymer has better long term cyclic stability than the PK. It can be concluded that the $\text{K}_3[\text{Fe}(\text{CN})_6]$ not only increase the specific capacitance of supercapacitor, but also scarcely impede the stability of supercapacitor, and the PKF can be considered as a promising gel polymer in supercapacitor.

4. Conclusions

In summary, we have prepared a solid-state supercapacitor utilized activated carbon as electrode and PVA–KOH– $\text{K}_3[\text{Fe}(\text{CN})_6]$ gel polymer as electrolyte and separator. With the contribution of redox reaction of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and its quick electron relay at the electrode|electrolyte interface, the supercapacitor shows excellent electrochemical performance, such as, high ionic conductivity of 45.6 mS cm^{-1} , high electrode specific capacitance of 430.95 F g^{-1} , high energy density of 57.94 Wh kg^{-1} , and excellent cycle life that maintains 89.3% of the initial capacitance values after 1000 cycles. The results show that the $\text{K}_3[\text{Fe}(\text{CN})_6]$ can improve the ionic conductivity and pseudocapacitance, therefore enhances the performance of the solid-state supercapacitor. This approach may provide a facile and easily scalable strategy to fabricate flexible and lightweight supercapacitor.

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References

- [1] A.K. Shukla, S. Sampath, K. Vijayamohanan, *Curr. Sci.* 79 (2000) 1656–1666.
- [2] M. Winter, R.J. Brodd, *Chem. Rev.* 104 (2004) 4245–4269.
- [3] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845–854.
- [4] J. Mua, G. Ma, H. Peng, J. Li, K. Sun, Z. Lei, *J. Power Sources* 242 (2013) 797–802.
- [5] G.J. Wang, L. Zhang, J.J. Zhang, *Chem. Soc. Rev.* 41 (2012) 797–828.
- [6] H. Yu, J. Wu, L. Fan, Y. Lin, K. Xu, Z. Tang, C. Cheng, S. Tang, J. Lin, M. Huang, Z. Lan, *J. Power Sources* 198 (2012) 402–407.
- [7] Y.G. Wang, X.G. Zhang, *Solid State Ionics* 166 (2004) 61–67.

[8] S. Yamazakia, A. Takegawab, Y. Kanekob, J. Kadokawab, M. Yamagataa, M. Ishikawa, *Electrochim. Commun.* 11 (2009) 68–70.

[9] Y. Kumar, G.P. Pandey, S.A. Hashmi, *J. Phys. Chem. C* 116 (2012) 26118–26127.

[10] G. Ma, H. Peng, J. Mu, H. Huang, X. Zhou, Z. Lei, *J. Power Sources* 229 (2013) 72–78.

[11] S. Sarangapani, B.V. Tilak, C.P. Chen, *J. Electrochem. Soc.* 143 (1996) 3791–3799.

[12] M.D. Ingram, H. Staesche, K.S. Ryder, *J. Power Sources* 129 (2004) 107–112.

[13] W.H. Meyer, *Adv. Mater.* 10 (1998) 439–448.

[14] G.B. Appetecchia, F. Crocea, P. Romagnolia, B. Scrosatia, U. Heiderb, R. Oesten, *Electrochim. Commun.* 1 (1999) 83–86.

[15] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Mater.* 2 (2003) 402–407.

[16] J. Wu, Z. Lan, J. Lin, M. Huang, S. Hao, T. Sato, S. Yin, *Adv. Mater.* 19 (2007) 4006–4011.

[17] H. Yu, J. Wu, L. Fan, K. Xu, X. Zhong, Y. Lin, J. Lin, *Electrochim. Acta* 56 (2011) 6881–6886.

[18] P. Sivaraman, R.K. Kushwaha, K. Shashidhara, V.R. Hande, A.P. Thakur, A.B. Samui, M.M. Khandpekar, *Electrochim. Acta* 55 (2010) 2451–2456.

[19] S.A. Hashmi, R.J. Latham, R.G. Linford, W.S. Schlindwein, *Polym. Int.* 47 (1998) 28–33.

[20] C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, *Nano Lett.* 10 (2010) 4025–4031.

[21] D.F. Vieira, C.O. Avellaneda, A. Pawlicka, *Electrochim. Acta* 53 (2007) 1404–1408.

[22] K. Lee, N. Wu, *J. Power Sources* 179 (2008) 430–434.

[23] S. Saricilar (Zengin), D. Antiohos, K. Shu, P.G. Whitten, K. Wagner, C. Wang, G.G. Wallace, *Electrochim. Commun.* 32 (2013) 47–50.

[24] C. Yang, S. Hsu, W. Chien, *J. Power Sources* 152 (2005) 303–310.

[25] J.M. Nugent, K.S.V. Santhanam, A. Rubio, P.M. Ajayan, *Nano Lett.* 1 (2001) 87–91.

[26] O.W. Brown, C.O. Henke, I.L. Miller, *J. Phys. Chem.* 24 (1920) 230–237.

[27] J. Okuno, K. Maehashi, K. Matsumoto, K. Kerman, Y. Takamura, E. Tamiya, *Electrochim. Commun.* 9 (2007) 13–18.

[28] H. Zhang, L. Wu, Q. Li, X. Du, *Anal. Chim. Acta* 628 (2008) 67–72.

[29] A.B. Syropoulos, A.C. Calokerinos, *Anal. Chim. Acta* 255 (1991) 403–411.

[30] J.X. Du, Y.H. Li, J.R. Lu, *Talanta* 55 (2001) 1055–1058.

[31] D. He, Z. Zhang, Y. Huang, Y. Hu, *Food Chem.* 101 (2007) 667–672.

[32] H. Lee, S. Lee, *Electrochim. Commun.* 6 (2004) 465–469.

[33] Z. Shao, I. Hsing, H. Zhang, B. Yi, *Int. J. Energy Res.* 30 (2006) 1216–1227.

[34] R. Kötz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483–2498.

[35] D. Hulicova-Jurcakova, A. Puziy, O. Poddubnaya, F. Suarez-Garcia, J. Tascon, G. Lu, *J. Am. Chem. Soc.* 131 (2009) 5026–5027.

[36] S. Prabaharan, R. Vimala, Z. Zainal, *J. Power Sources* 161 (2006) 730–736.

[37] M.F.Z. Kadir, S.R. Majid, A.K. Arof, *Electrochim. Acta* 55 (2010) 1475–1482.

[38] P. Jannasch, *Polymer* 42 (2001) 8629–8635.

[39] G. Lota, E. Frackowiak, *Electrochim. Commun.* 11 (2009) 87–90.

[40] L.H. Su, X.G. Zhang, C.H. Mi, B. Gao, Y. Liu, *Phys. Chem. Chem. Phys.* 11 (2009) 2195–2202.

[41] S.T. Senthilkumar, R. Kalai Selvan, Y.S. Lee, J.S. Melo, *J. Mater. Chem. A* 1 (2013) 1086–1095.

[42] M. Hughes, G. Chen, M. Shaffer, D. Fray, A. Windle, *Chem. Mater.* 14 (2002) 1610–1613.

[43] J. Wang, Y. Xu, F. Yan, J. Zhu, J. Wang, *J. Power Sources* 196 (2011) 2373–2379.

[44] P.L. Taberna, P. Simon, J.F. Fauvarque, *J. Electrochem. Soc.* 150 (2003) A292–A300.

[45] E. Frackowiak, *Appl. Phys. Lett.* 77 (2000) 2421–2423.